

Docket No.: K-0597

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Customer No.: 34610

Jeong Dae SEO; Kyung Hoon LEE; Hee Jung KIM; Chun Gun PARK and Hyoung Yun OH

Confirmation No: 9463

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Group Art: 1774

Filed: December 24, 2003

Examiner: Camie S. Thompson

For: ORGANIC ELECTROLUMINESCENT DEVICE

TRANSMITTAL OF CERTIFIED PRIORITY DOCUMENT(S)

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Sir:

At the time the above application was filed, priority was claimed based on the following application(s):

**Korean Patent Application No. 10-2002-0083279 filed December 24, 2002**

A copy of each priority application listed above is enclosed.

Respectfully submitted,  
FLESHNER & KIM, LLP



Daniel Y.J. Kim  
Registration No. 36,186  
Daniel S. Kim  
Registration No. 51,877

P.O. Box 221200  
Chantilly, Virginia 20153-1200  
703 766-3701 DYK/DSK/krf

**Date: November 28, 2005**


**Please direct all correspondence to Customer Number 34610**



## CERTIFICATE OF VERIFICATION

I, Sung Mi JEON of 648-23 Yeoksam-dong, Gangnam-gu, Seoul, Republic of Korea state that the attached document is a true and complete translation to the best of my knowledge of the Korean-English language and that the writings contained in the following pages are correct English translation of the specification and claims of the Korean Patent Application No. 10-2002-0083279

Dated this 24 day of December, 2005.

Signature of translator: 

Sung Mi JEON

# **KOREAN INTELLECTUAL PROPERTY OFFICE**

This is to certify that the following application annexed hereto is a  
  
true copy from the records of the Korean Industrial Property Office.

Application Number: Patent Application No. 2002-0083279

Date of Application: December 24, 2002

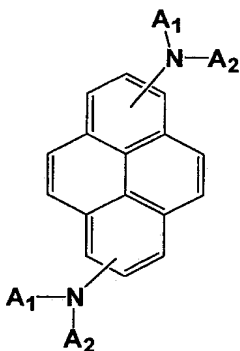
Applicant(s): LG Electronics Inc.

**COMMISSIONER**

**[ABSTRACT OF THE DISCLOSURE]****[ABSTRACT]**

Disclosed is an organic electroluminescent device including an emitting layer formed of a blue luminescent material having a high color purity, and more particularly to an organic electroluminescent device having an emitting layer formed between an electron-injected electrode (anode) and a hole-injected electrode (cathode), the layer using the blue emitting material being expressed by the following chemical formula 1 as a dopant:

[Chemical formula 1]

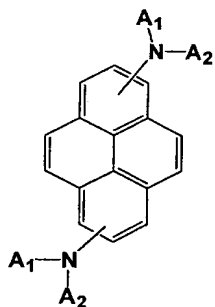
**[INDEX WORDS]**

Blue emitting material, organic electroluminescent device, color purity

**[SPECIFICATION]****[TITLE OF THE INVENTION]****ORGANIC ELECTROLUMINESCENT DEVICE****[DETAILED DESCRIPTION OF THE INVENTION]****[OBJECT OF THE INVENTION]****[FIELD OF THE INVENTION AND DISCUSSION OF THE RELATED ART]**

The present invention relates to an organic electroluminescent device, and more particularly, to a blue emitting material of an emitting layer using a chemical formula 1 as a dopant.

[Chemical formula 1]



Recently, with the trend of a large sized display, a request of a flat display that occupies a small area has been increased. One example of the flat display is an organic electroluminescent device also called as an organic light emitting diode (OLED). And, technology for the organic electroluminescent display is developed rapidly, whereby various prototypes have been in market already.

The organic electroluminescent device emits light in a manner that electric charges are injected in an organic layer formed between an anode and a cathode so as to form a pair of electron and hole to generate an exciton and an excited state of the exciton falls to a ground state so as to emit light. The organic electroluminescent device

is not only formed on a flexible transparent substrate such as a plastic but also operated at a lower voltage (less than 10V) compared to a plasma display panel or an inorganic electroluminescent display. Also, the organic electroluminescent device has advantages in that power consumption is reduced and various colors are available.

Moreover, the organic electroluminescent device enables to express three colors including green, blue, and red. Therefore, many concerns are focused on the organic electroluminescent device as the next generation full color display. However, it is a biggest problem in realizing blue luminescence of the organic electroluminescent device that a degree of color purity and the luminescence efficiency are lowered.

Here, the procedure of fabricating an organic electroluminescent device will be described briefly.

(1) Firstly, an anode material is coated on a transparent substrate. Indium tin oxide (ITO) is often used as the anode material.

(2) A hole injecting layer(HIL) is coated thereon. Copper phthalocyanine(CuPC)is mainly used as the hole injecting layer at a thickness of 10 to 30nm.

(3) Then, a hole transport layer(HTL) is coated. 4,4'-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl(NPB) is deposited and coated at 30 to 60nm as the hole transport layer.

(4) An organic emitting layer is formed thereon. At this moment, a dopant is added thereto as needed. In case of green luminescence, tris(8-hydroxy-quinolate)aluminum(Alq3) is deposited at a thickness of 30 to 60nm as the organic emitting layer, and MQD(N-methyl quinacridone) is commonly used as the dopant.

(5) An electron transport layer (ETL) or electron injecting layer(EIL) are consecutively coated thereon, or an electron injecting transport layer is formed thereon.

In case of green luminescence, Alq<sub>3</sub> of the above (4) has a good electron transport capability, and thus it is often the case that no electron injecting/transport layer is used.

(6) Next, a cathode is coated, and finally a protecting layer is coated.

The organic electroluminescent device may be realized to emit blue, green, or red light in accordance with a material forming the emitting layer.

Particularly, the emitting layer for blue luminescence is a host employing materials of blue dopants and is fabricated by doping metallic materials such as perylene, coumarine, pyrene and their derivatives such as BAlq as a dopant. However, it is a biggest problem in realizing blue luminescence of the organic electroluminescent device that a degree of color purity and the luminescence efficiency are lowered.

The conventional blue emitting materials emit light with a long wavelength during emission and had a problem of lowering the degree of color purity and the luminescence efficiency, and even more lowered at high doping density.

#### **[TECHNICAL TASKS TO BE ACHIEVED BY THE INVENTION]**

Accordingly, the present invention is directed to an organic electroluminescent device that substantially obviates one or more problems due to limitations and disadvantages of the related art.

An object of the present invention is to provide an organic electroluminescent device having a high degree of color purity in realizing blue luminescence by synthesizing a novel blue material therein.

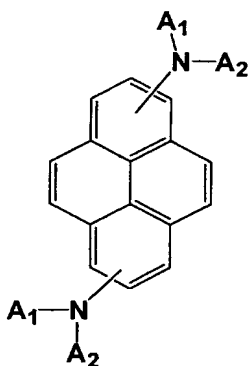
Additional advantages, objects, and features of the invention will be set forth in part in the description which follows and in part will become apparent to those having ordinary skill in the art upon examination of the following or may be learned from practice of the invention. The objectives and other advantages of the invention may be realized and attained by the structure particularly pointed out in the written description

and claims hereof as well as the appended drawings.

### [PREFERRED EMBODIMENTS OF THE INVENTION]

To achieve these objects and other advantages and in accordance with the purpose of the invention, as embodied and broadly described herein, organic electroluminescent device of the present invention embracing an anode, a hole injecting layer, a hole transport layer, an emitting layer, a hole blocking layer, an electron transport layer, an electron injecting layer and a cathode uses a material as a luminescent material, the material being expressed by the following chemical formula 1:

[Chemical formula 1]



The material expressed in the chemical formula 1 can be used solely or composed with more than one material. A wt% of the material in the chemical formula 1 is 0.1 ~ 90wt% among a total weight of the emitting layer.

The material to be composed to the material in the chemical formula 1, for being used as a luminescent layer, is selected from a substituted or non-substituted fused aromatic group consisting of naphthalene, anthracene, phenanthrene, pyrene, perylene, quinoline and acridone.

Also, the substituted group is selected from a group consisting of aryl, arylallyl, allyl, alkyl, alkoxy, aryloxy and arylamino.

In the above chemical formula, at least one of an A<sub>1</sub> and A<sub>2</sub> is selected from a

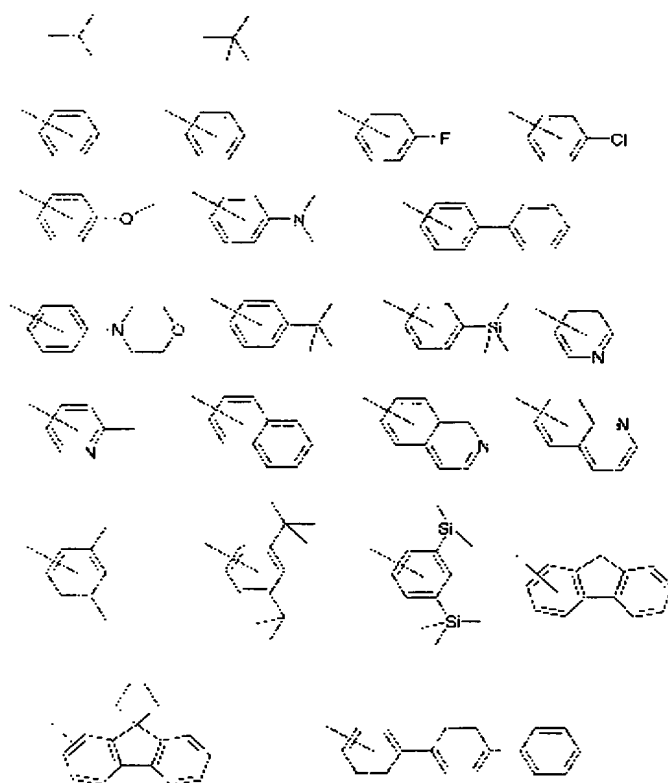


substituted or non-substituted aromatic group, a hetero ring group, an aliphatic group or hydrogen, e.g., the substituent of each substituted A1 and A2 is selected from the substituted group consisting of aryloxy, alkoxy, alkyl, alkylamino, hydroxyl, amino, halogen, carbonyl, amide, alkylsilyl, arylsilyl and carboxylic, respectively.

Moreover, the substituent of each substituted A1 and A2 is at least one and selected from a group consisting of phenoxy, tolyloxy, vinyl, aldehyde, methyl, ethyl, propyl, i-propyl, t-butyl, cyclohexyl, diphenylamino, methoxy, ethoxy, propoxy, butoxy, dimethylamino, trimethylsilyl, triphenylsilyl, carboxylic acid group, fluorine and chlorine.

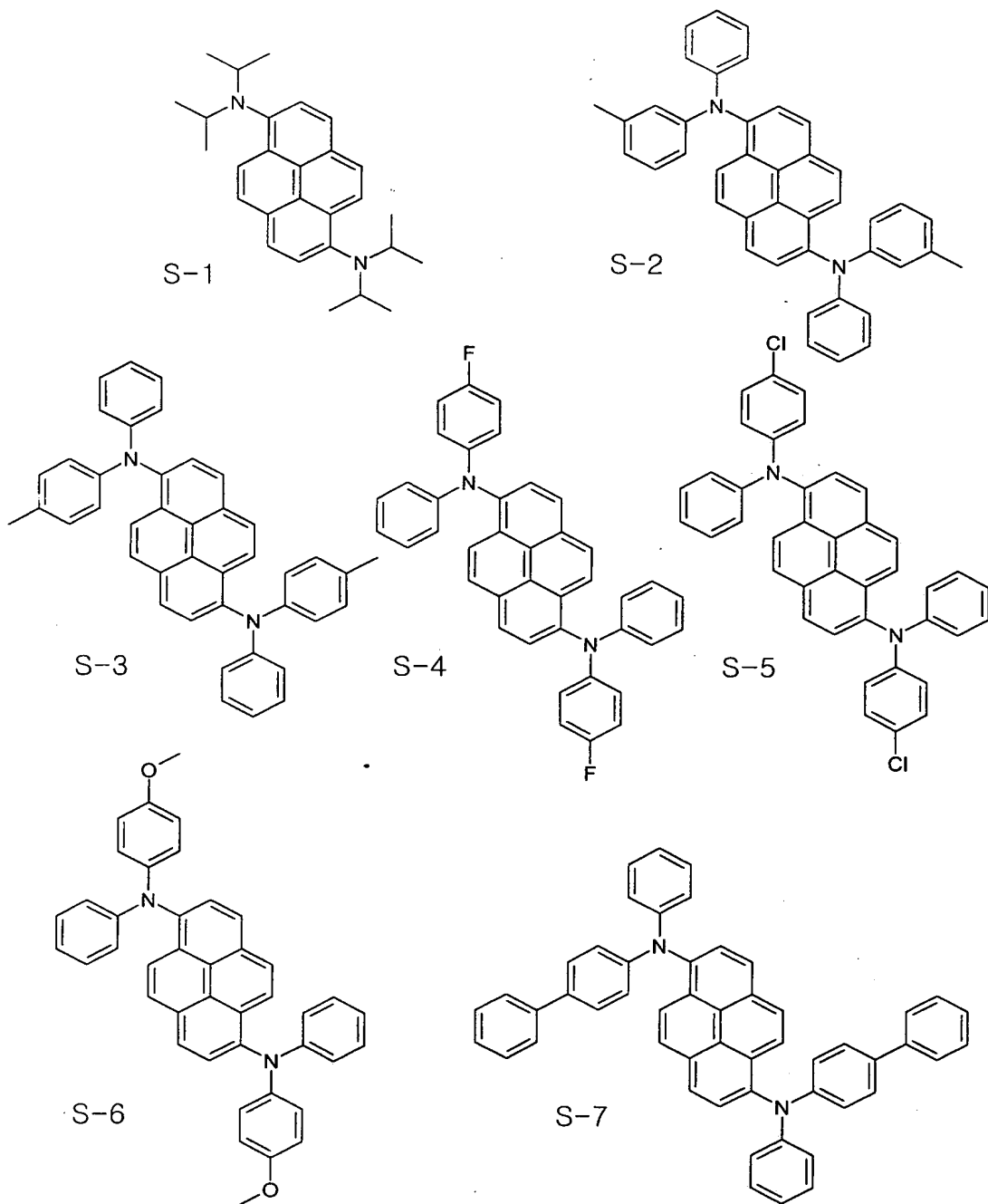
The substituent of each substituted A1 and A2 can be selected from a functional group expressed by the following chemical formula 2:

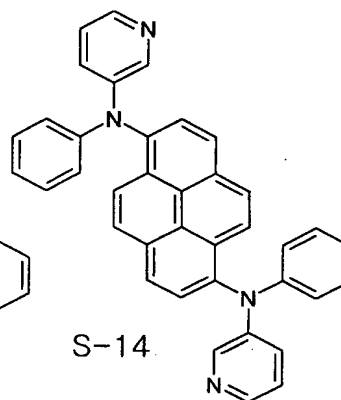
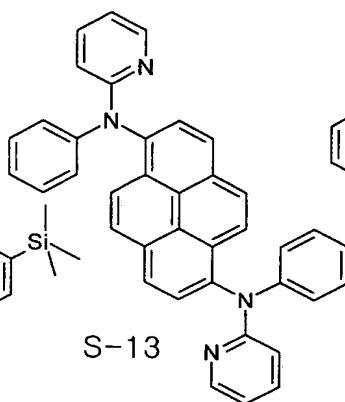
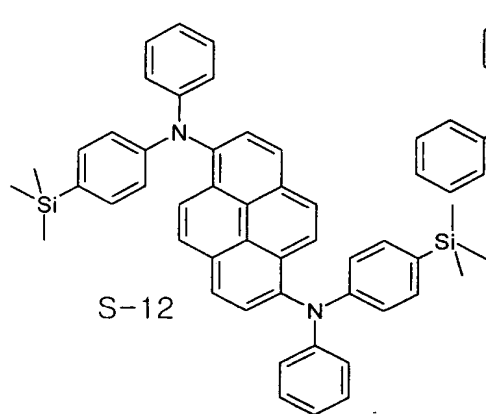
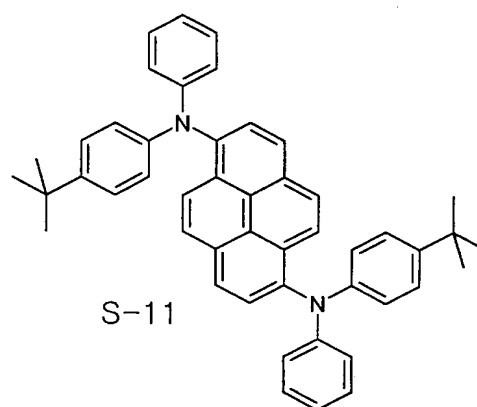
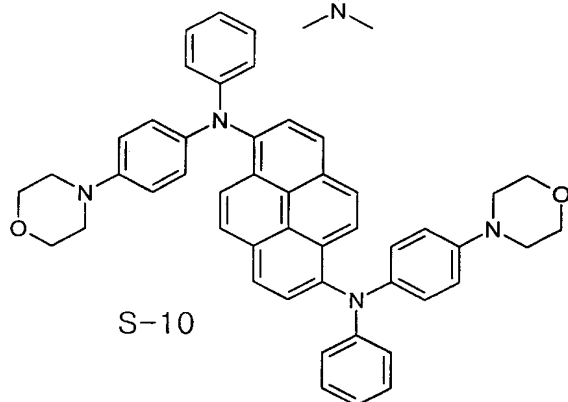
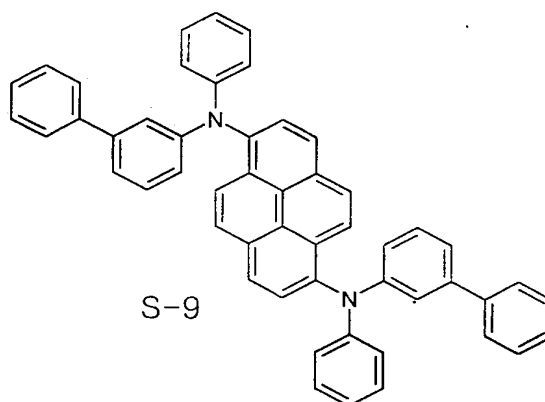
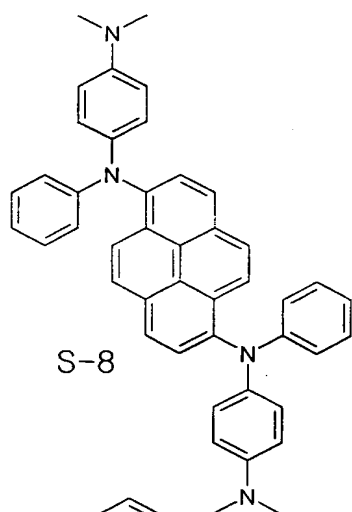
[Chemical formula 2]

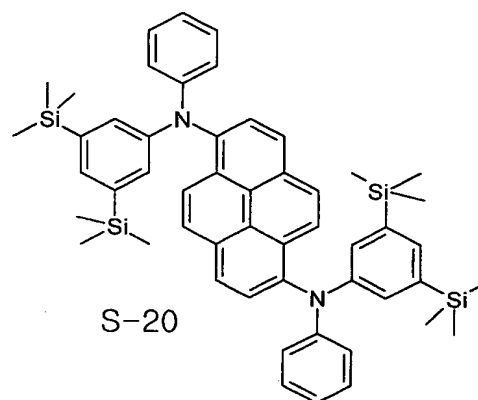
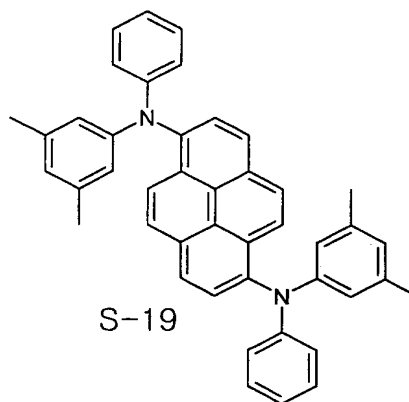
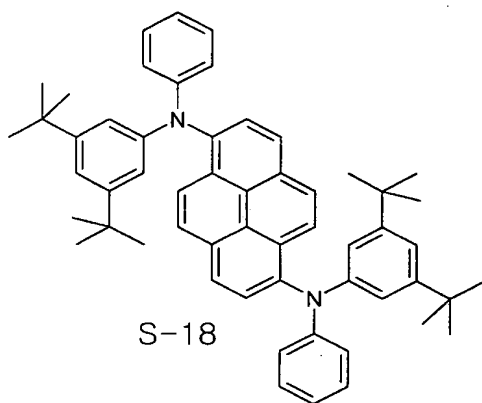
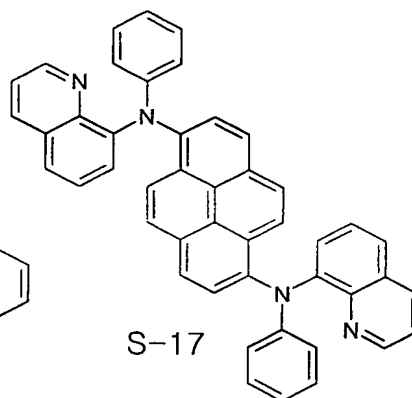
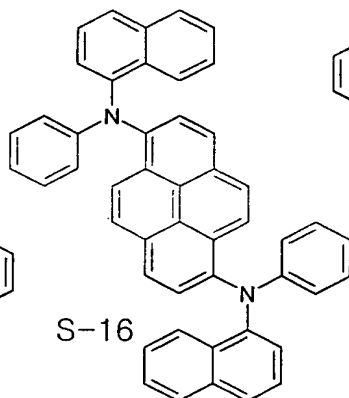
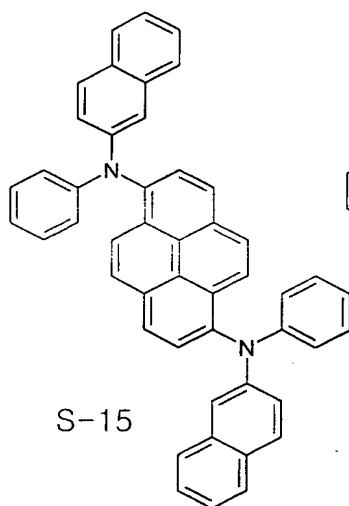


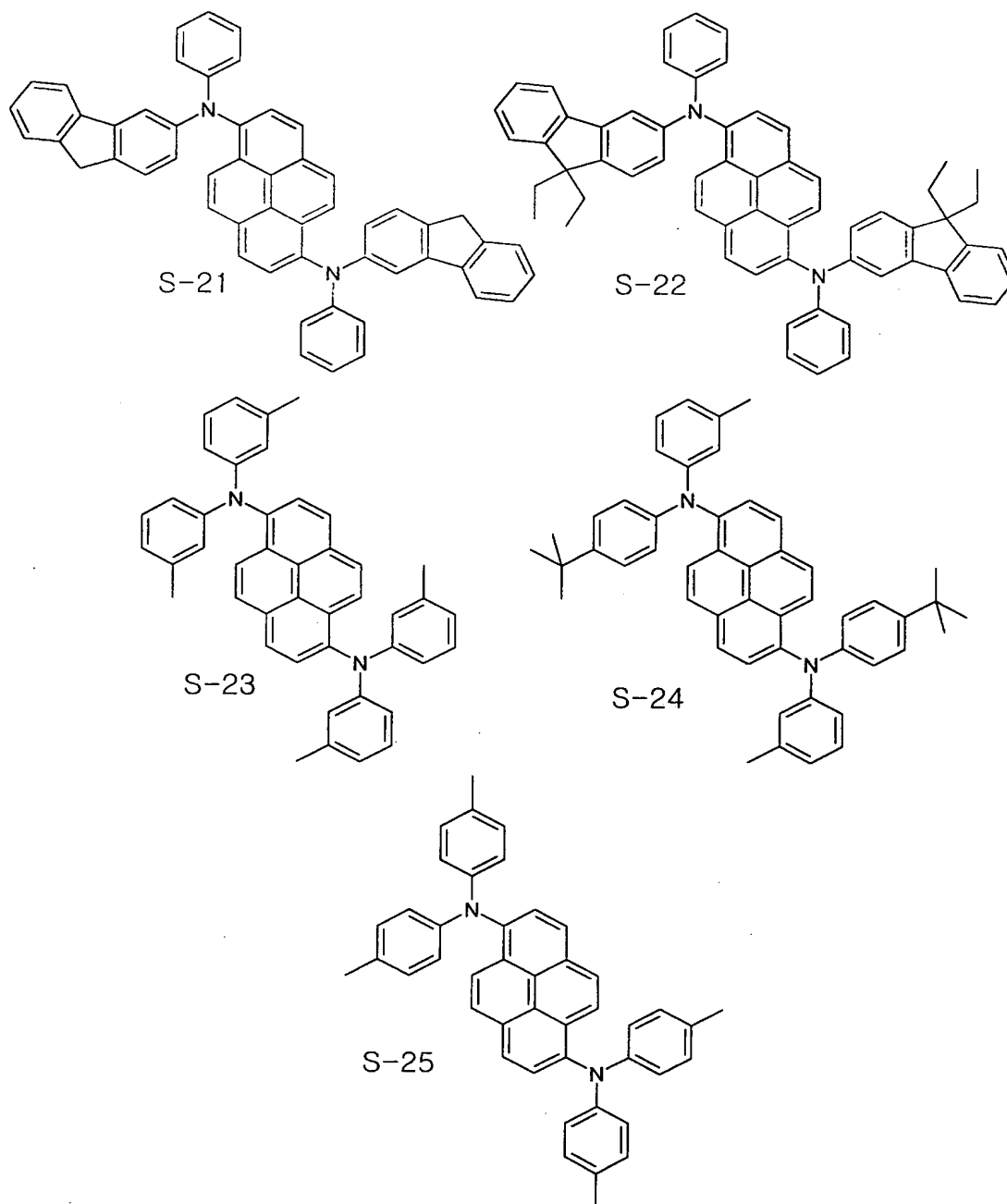
And the chemical formula 1 having the above substituent A1 and A2 has the same structure as chemical formula 3 which will be expressed in the following.

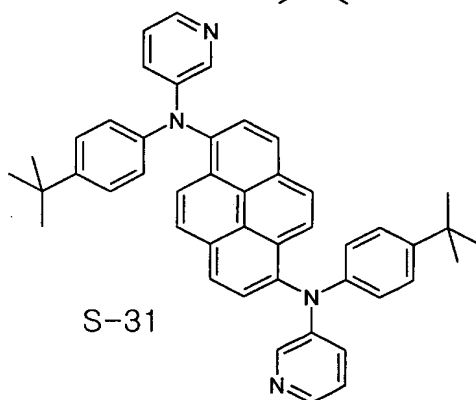
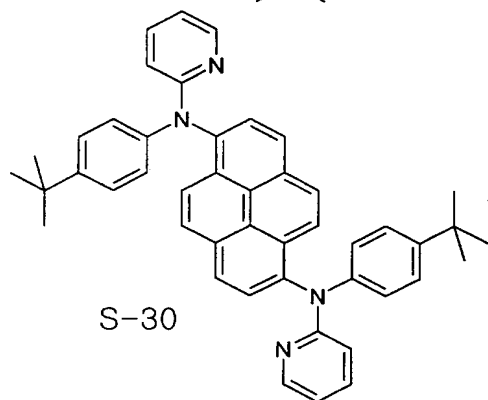
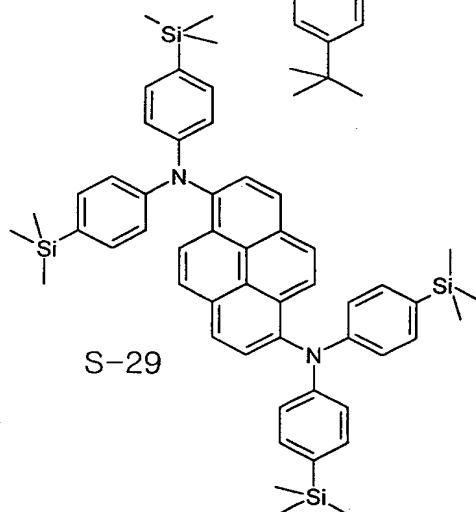
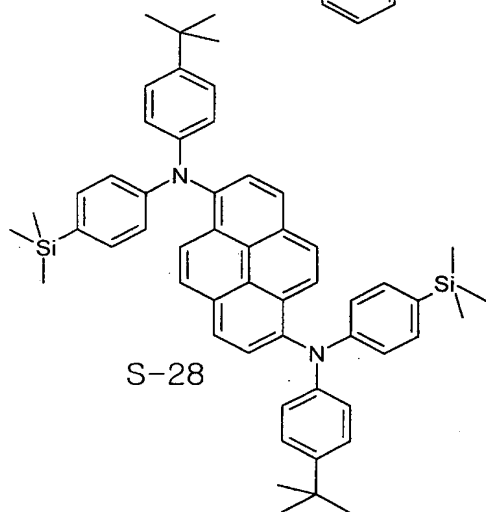
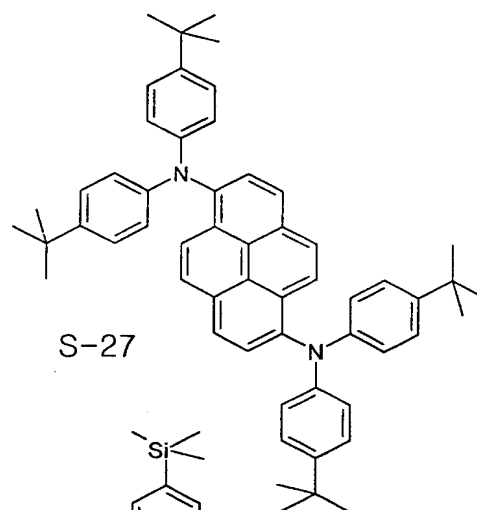
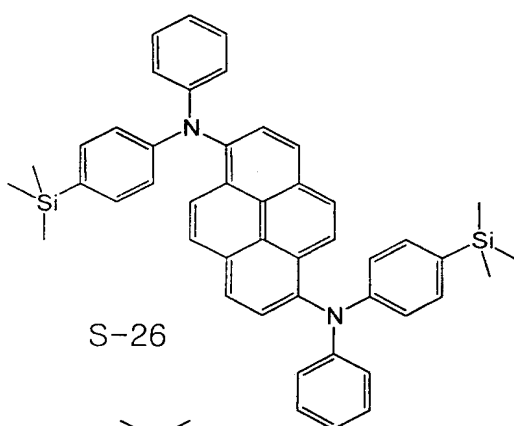
[Chemical formula 3]

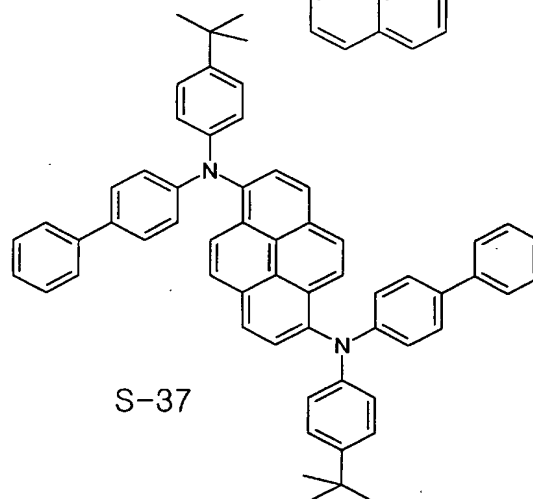
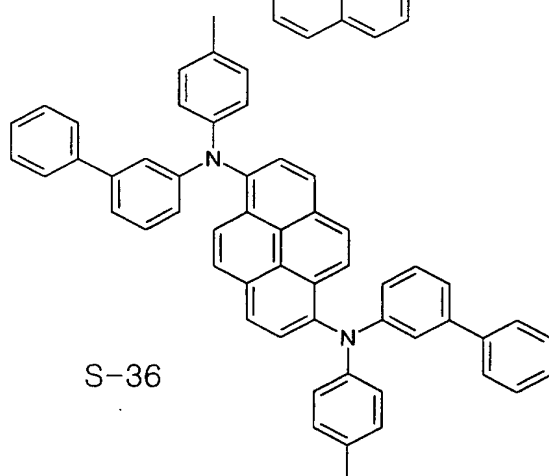
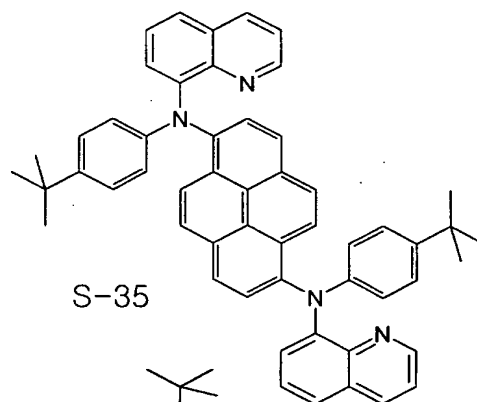
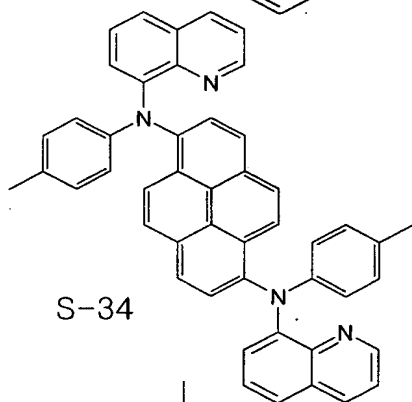
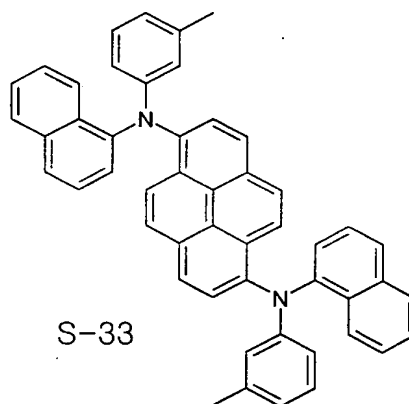
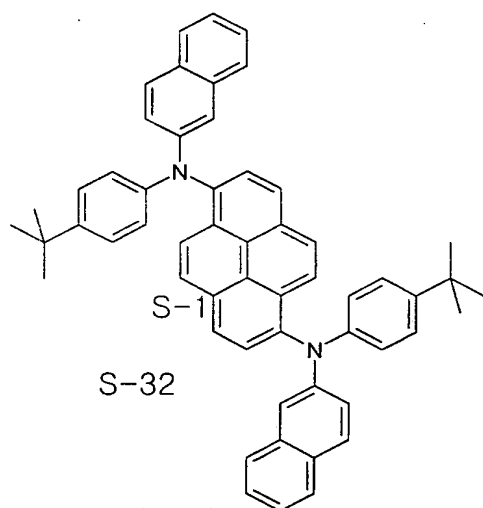


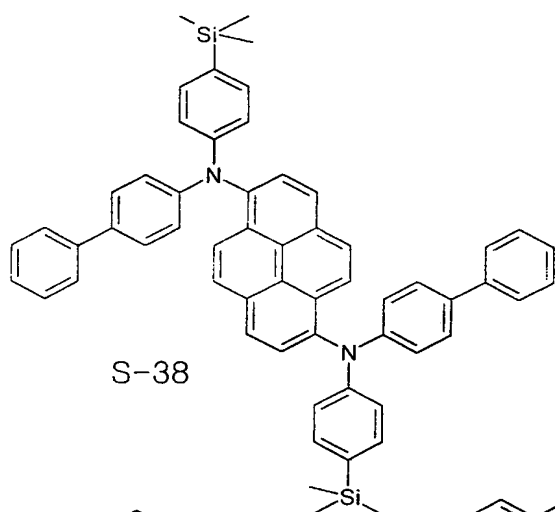




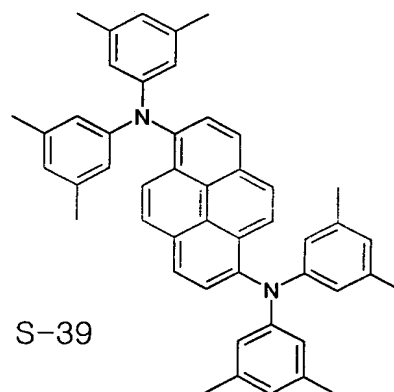




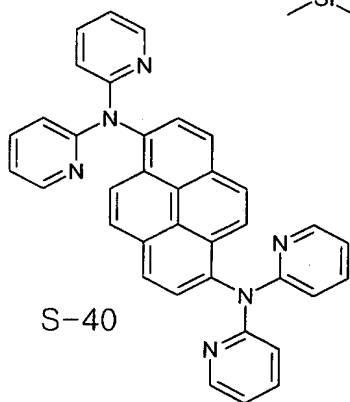




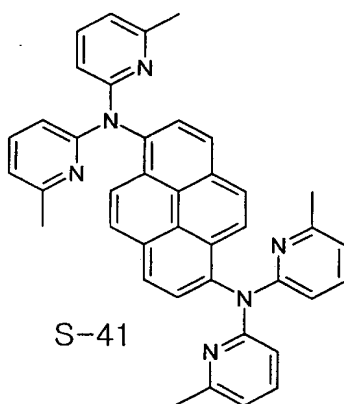
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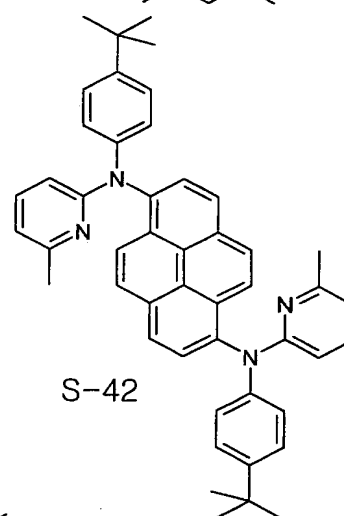
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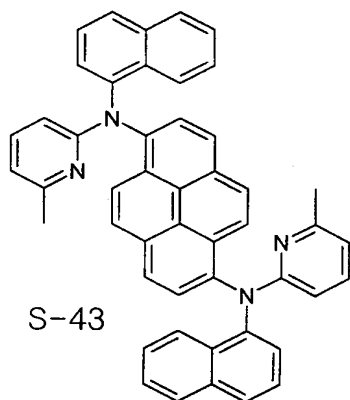
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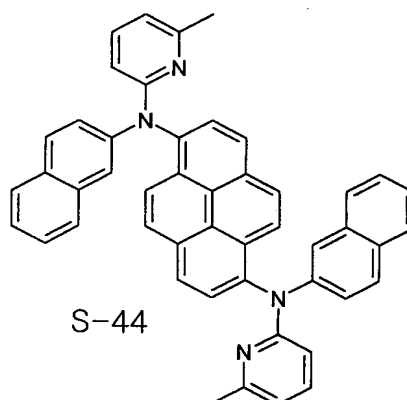
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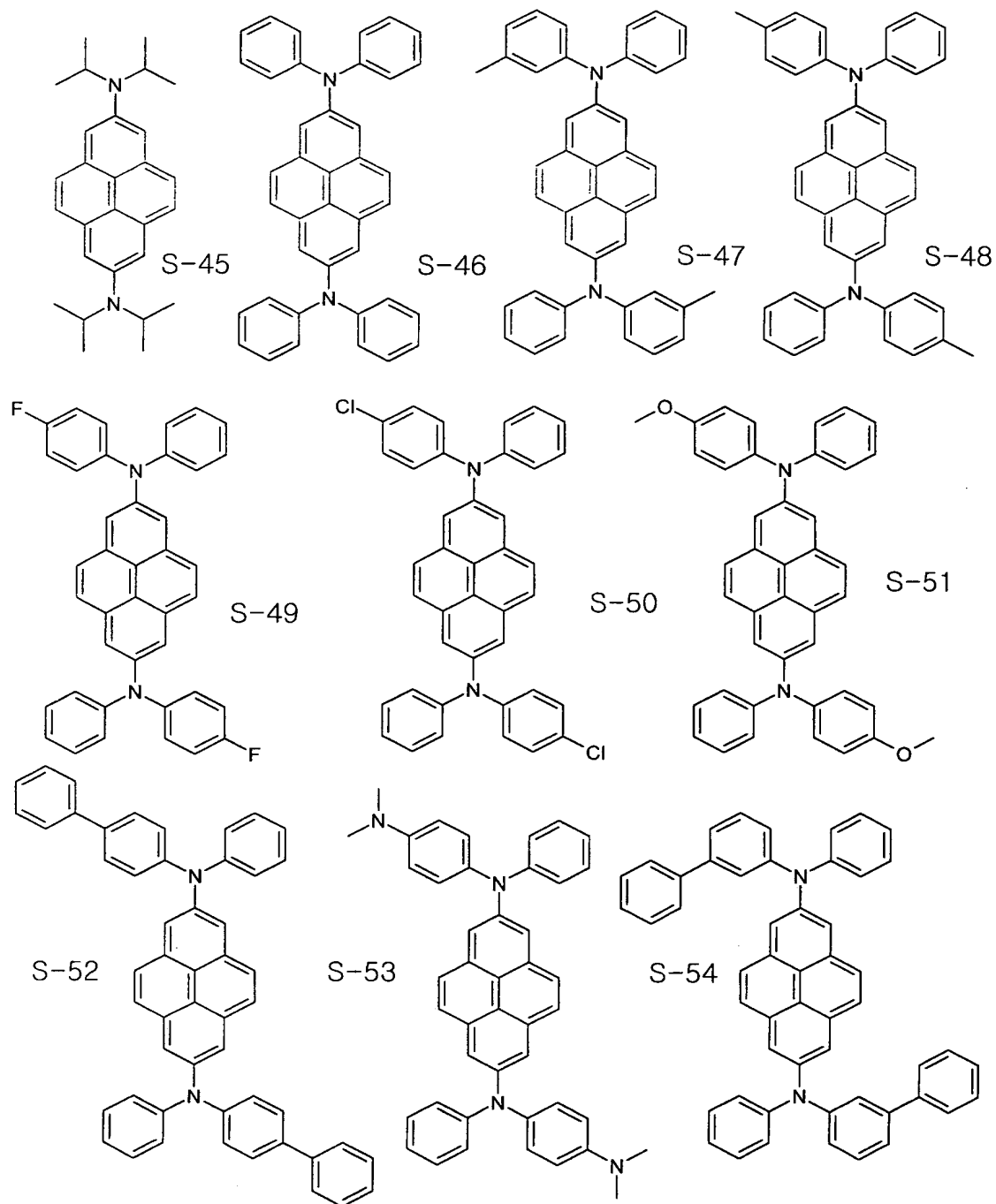


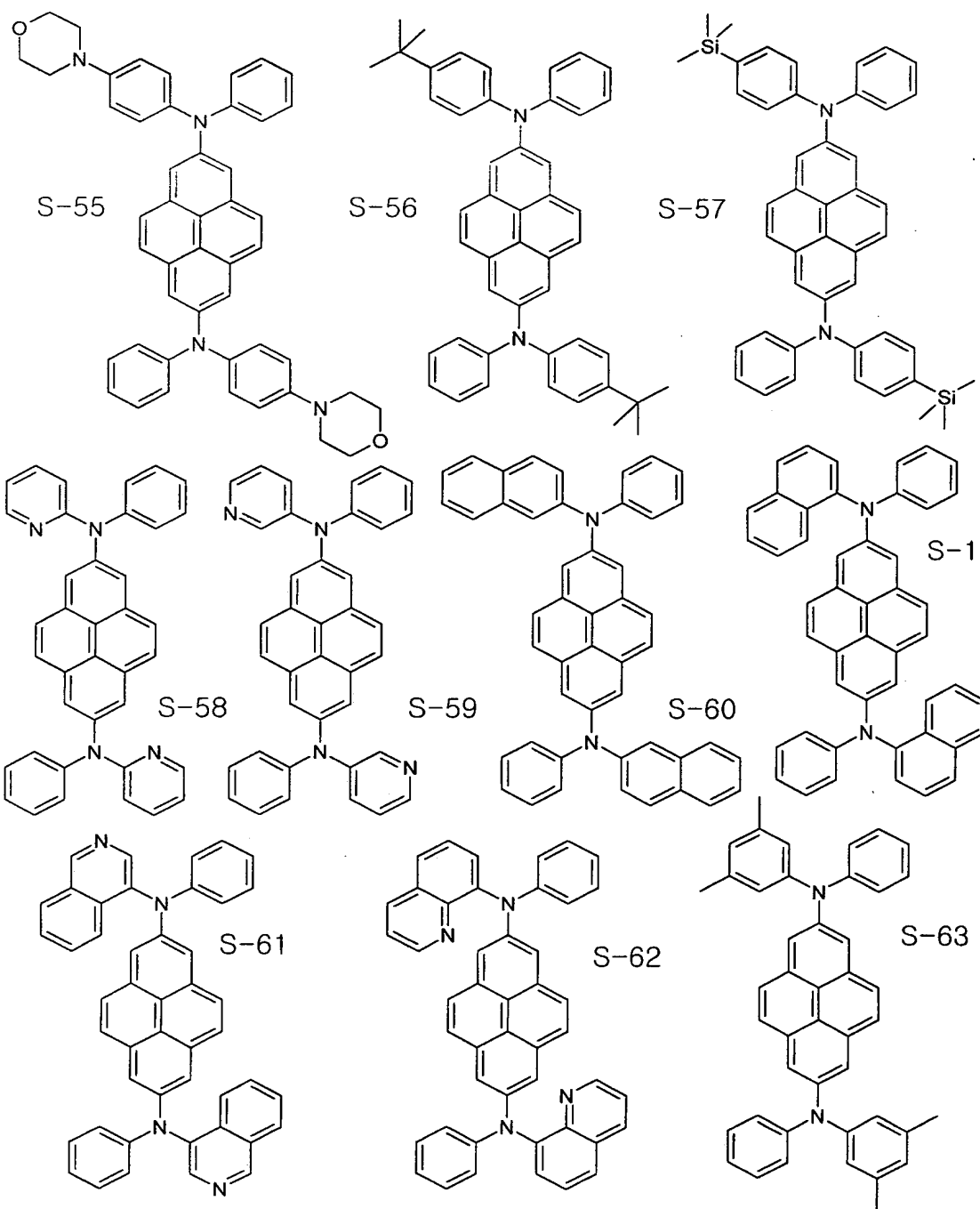
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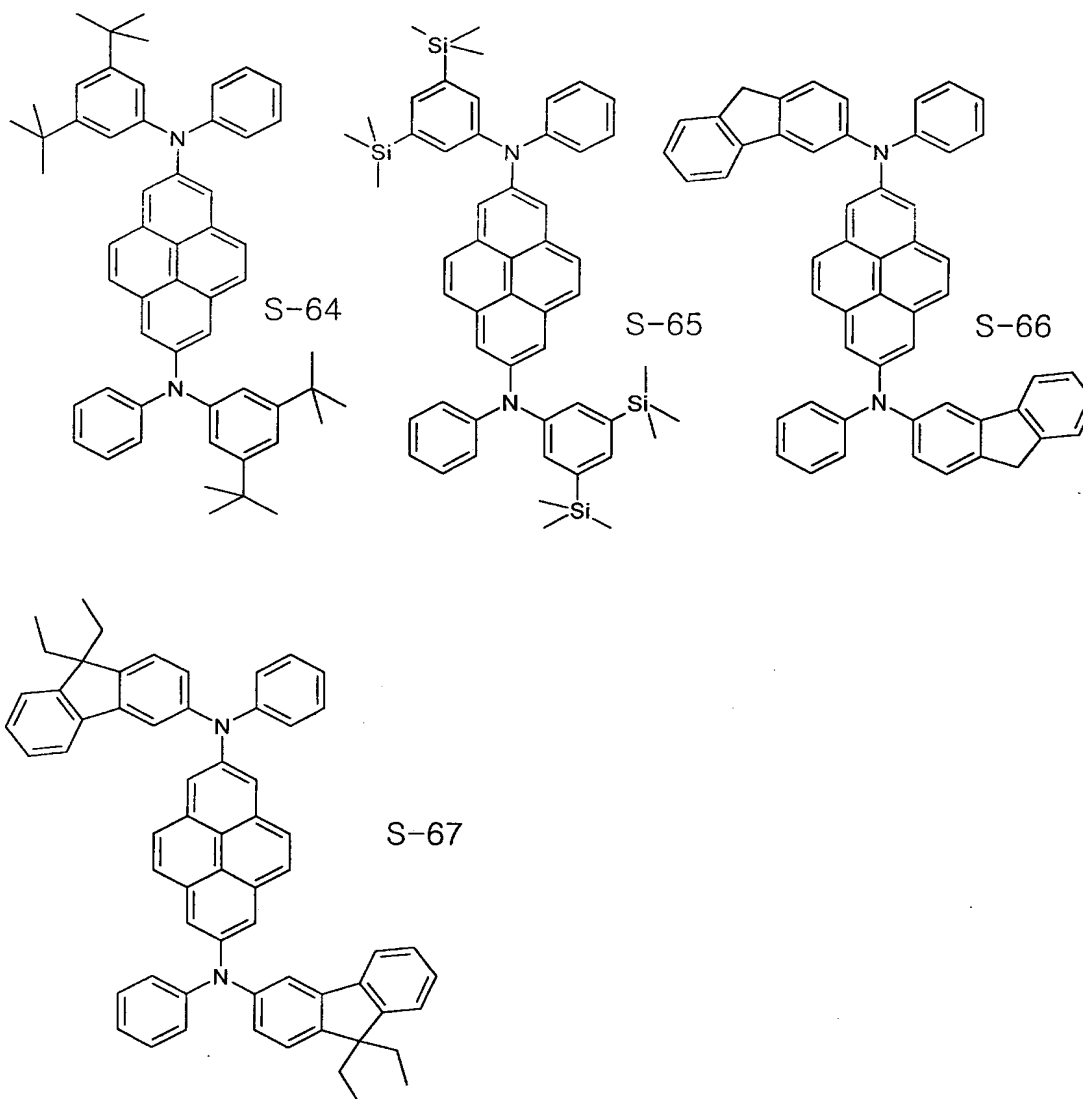


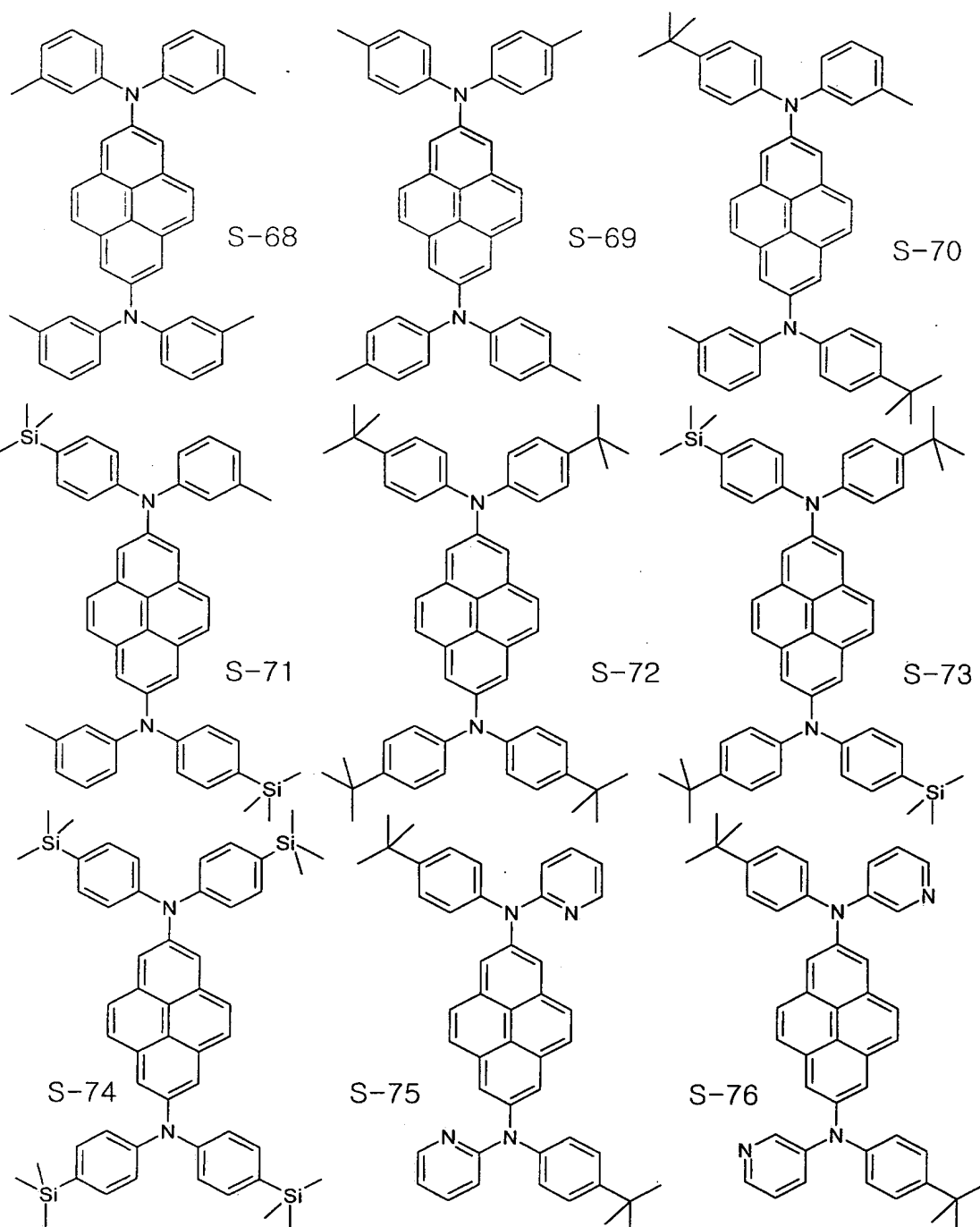
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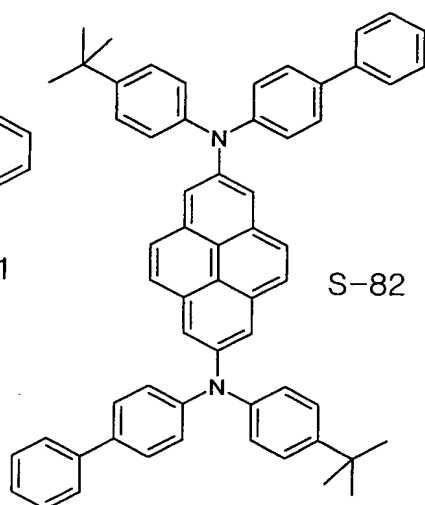
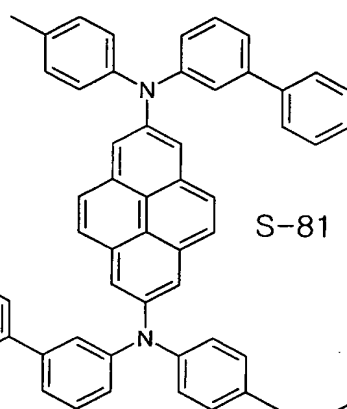
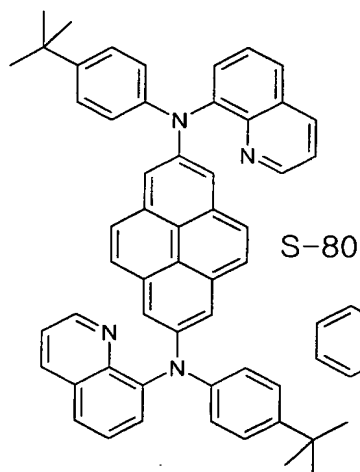
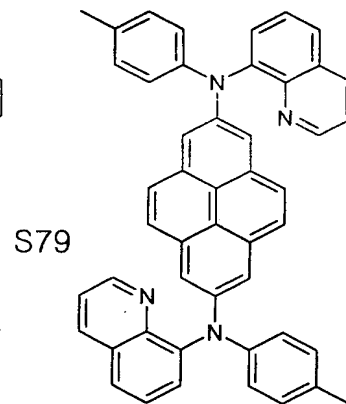
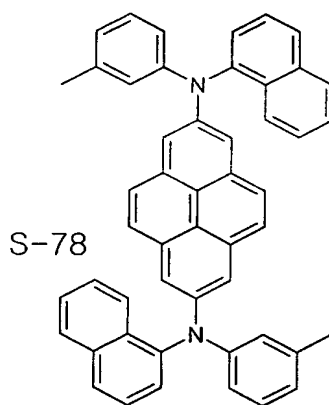
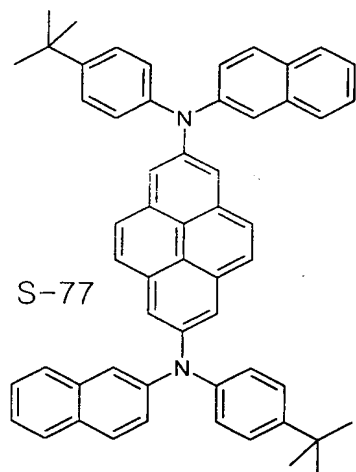


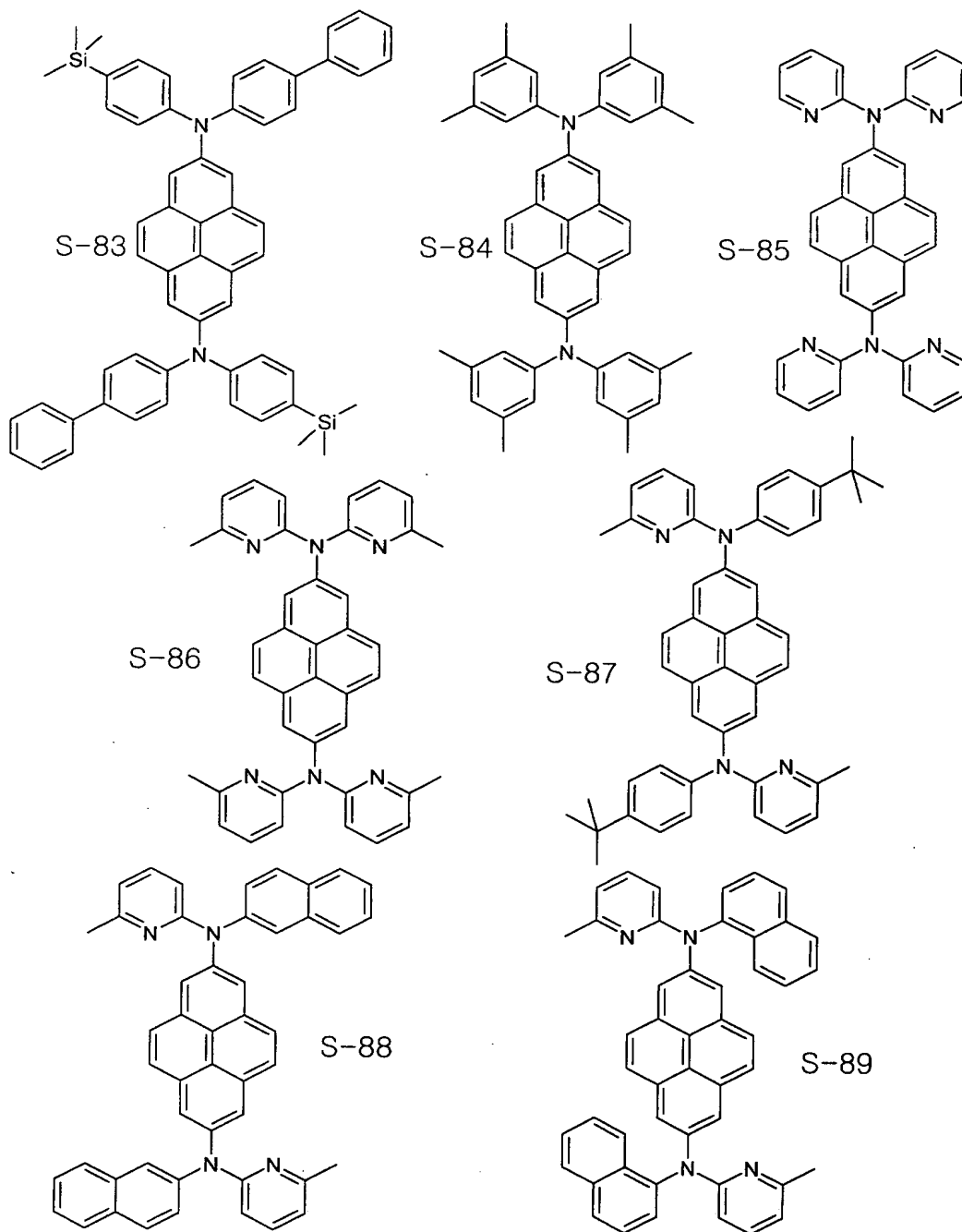






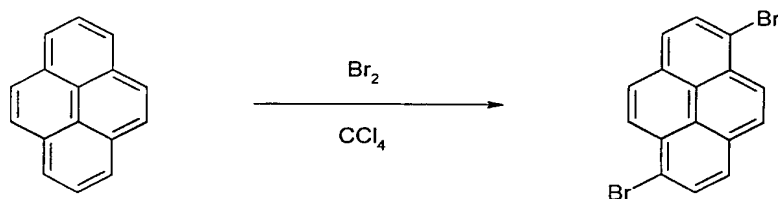






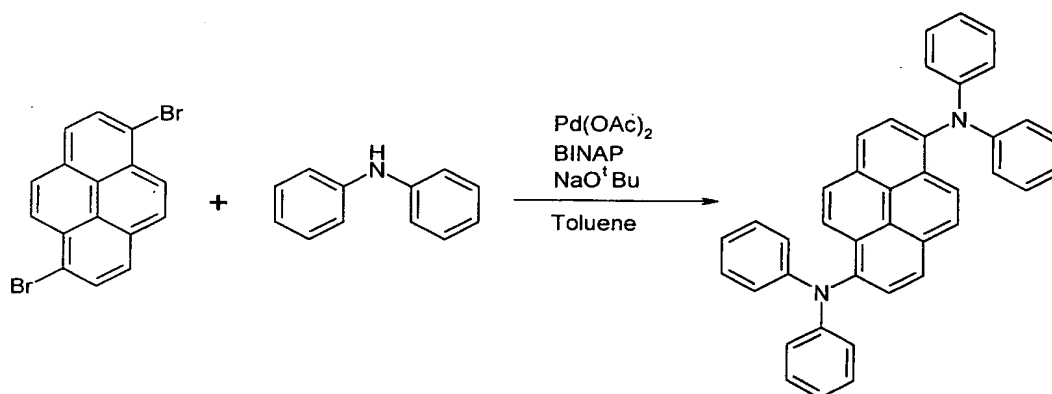
According to the organic electroluminescent device, N,N'-Bis-(4-tert-butyl-phenyl)-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine employed as the blue emitting material is compounded as follows.

(1) Synthesis of 1,6-Dibromopyrene



First, pyrene (10g, 0.0049mol) is dissolved into  $\text{CCl}_4$  (300mL) in a 3-necks-r.b.f. . And,  $\text{Br}_2$  (17.38g, 0.108mol) and  $\text{CCl}_4$  (50mL) are put into a dropping funnel provided at the round-floor flask and slowly dropped in the round-floor flask for 4 hours.  $\text{N}_2$  is added to and  $\text{HBr}$  is removed from the solution. When the process is finished, the solution is stirred under  $\text{N}_2$  current for one hour and formed sediment is filtered. When the sediment is recrystallized by toluene, a green solid matter (6.05g, 34%) of 1,6-Dibromopyrene and a white solid matter of 1,8-Dibromopyrene (5g, 28%) are obtained.

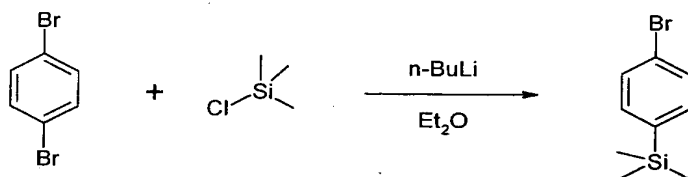
## (2) Synthesis of N,N,N',N'-Tetraphenyl-pyrene-1,6-diamine



First, 1,6-Dibromopyrene (3g, 0.0083mol), Diphenylamine (4.23g, 0.025mol), BINAP ([2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl]) (0.052g, 1% mol),  $\text{Pd}(\text{OAc})_2$  [Palladium(II) acetate] (0.019g, 1% mol) and  $\text{NaO}^t\text{Bu}$  [Sodium tert-butoxide] (2.3g, 0.029mol) are dissolved into toluene (80mL) in 2-necks-r.b.f. so as to be refluxed. When the reaction is finished, the 2-necks-r.b.f. is cooled at a normal temperature and about 40ml of toluene, that is, a reaction solvent is removed by

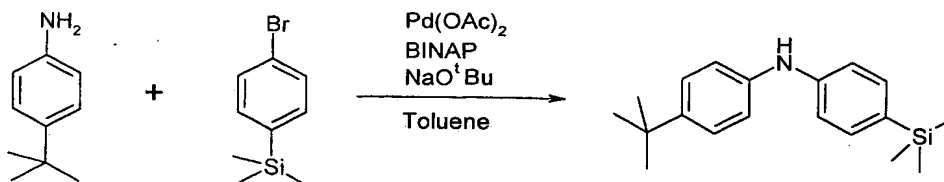
distillation under reduced pressure. When methanol (100ml) is added to the solution from which toluene 40ml is removed, sediment is generated. When the sediment is filtered, a yellow solid matter of N,N,N',N'-Tetraphenyl-pyrene-1,6-diamine (3.22g, 72%) is obtained..

### (3) Synthesis of (4-Bromo-phenyl)-trimethyl-silane



First, a dropping funnel is provided at the 3-necks-r.b.f. and the round-floor flask is dried under decompression. 1,4-Dibromobenzene (12,7g, 0.053mol) and the dried diethylether (300mL) are dissolved in the round-floor flask. A dryice bath is provided at the round-floor flask,  $n\text{-BuLi}$  (33,58mL, 0.0537mol) is put into the dropping funnel and  $n\text{-BuLi}$  is slowly dropped, and a temperature is slowly raised from  $-78^\circ\text{C}$  to  $0^\circ\text{C}$ . Next, chloro trimethylsilane (7,51mL, 0.059mol) is slowly dropped at  $0^\circ\text{C}$  and then the temperature is raised again to the normal temperature for over a period of one hour. When the reaction is finished, sediment is extracted by using diethylether and water is removed from the result by using  $\text{MgSO}_4$ . And then, after solvent is removed from the result, when the solvent is fractionally distilled under decompression, (4-Bromo-phenyl)-trimethyl-silane (11,3g, 92%) is obtained.

### (4) Synthesis of (4-tert-Butyl-phenyl)-(4-trimethylsilanyl-phenyl)-amine

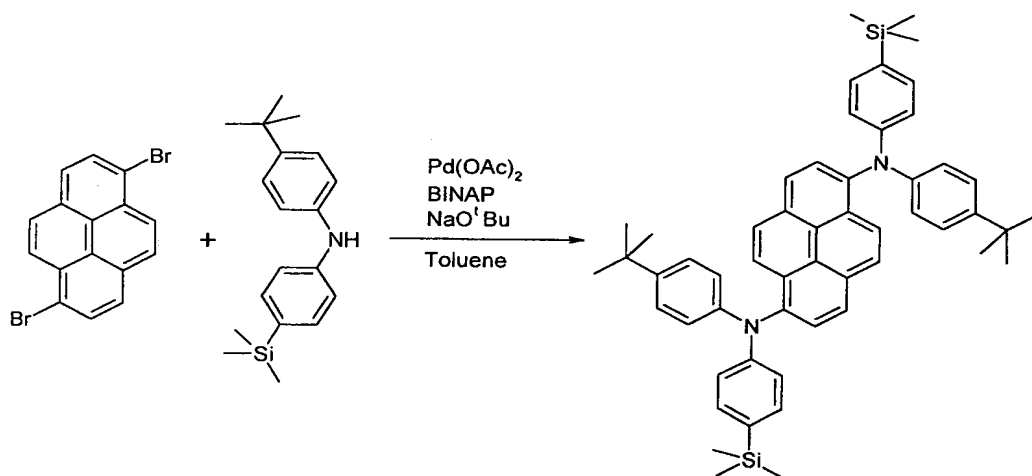


4-tert-Butyl-phenylamine (1.2mL, 0.0076mol), (4-Bromo-phenyl)-trimethyl-



silane(1g,0.0044mol), BINAP(0.03g, 1%mol),  $\text{Pd}(\text{OAc})_2$ (0.01g, 1%mol) and  $\text{NaO}^t\text{Bu}$ (1.5g, 0.016mol) are dissolved into toluene(50mL) in the 2-necks-r.b.f. so as to be refluxed for about 2 hours. When the reaction is finished, the 2-necks-r.b.f. is cooled and toluene, which is reaction solvent, is removed. Next, when the sediment is filtered, the white solid matter such as (4-tert-Butyl-phenyl)-(4-trimethylsilanyl-phenyl)-amine (1.12g, 86%) is obtained.

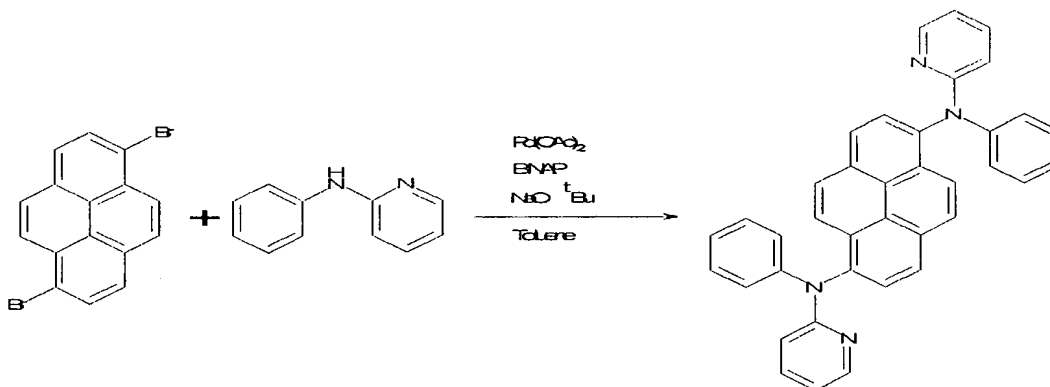
(5) Synthesis of N,N'-Bis-(4-tert-butyl-phenyl)-N,N'-bis-(4-trimethylsilanyl-phenyl)-pyrene-1,6-diamine



(1,6-Dibromopyrene)(0.787g, 0.0022mol), (4-tert-Butyl-phenyl)-(4-trimethylsilanyl-phenyl)-amine(1.56g, 0.00525mol), BINAP(0.054g, 4%mol),  $\text{Pd}(\text{OAc})_2$ (0.015g, 3%mol) and  $\text{NaO}^t\text{Bu}$ (0.93g, 0.0096mol) are dissolved in toluene (40mL) so as to be refluxed for 24 hours. When reaction is finished, the round-floor flask is cooled and result material is extracted by using water and methylene chloride after toluene, that is, the reaction solvent is removed. And then, water is removed from the result by using  $\text{MgSO}_4$  and methylene chloride is removed by decompression, and silica gel chromatography is separated by using n-hexane : methylene chloride (6:1). When the solvent is removed from the result and a solid matter is filtered by using

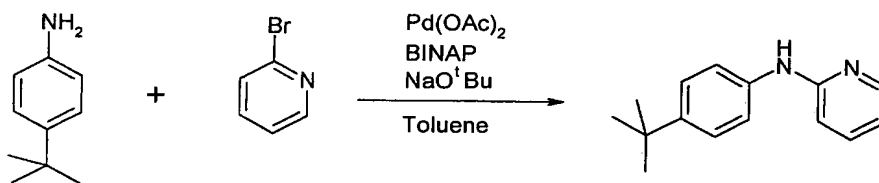
nucleic acid, yellow solid matter such as (N,N'-Bis-(4-tert-butyl-phenyl)-N,N'-bis-(4-trimethylsilyl-phenyl)-pyrene-1,6-diamine)(1.09g, 63%) is obtained..

(6) Synthesis of N,N'-Diphenyl-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine



(1,6-Dibromopyrene) (1.2g, 0.0033mol), (Phenyl-pyridin-2-yl-amine)(1.36g, 0.008 mol), BINAP(0.083g, 4%mol), Pd(OAc)<sub>2</sub>(0.022g, 3%mol) and NaO<sup>t</sup>Bu(1.28g, 0.013mol) are dissolved in toluene (50mL) in the 2-necks-r.b.f. so as to be refluxed for 24 hours. When the reaction is finished, solid matter is generated. When 50 % of toluene is removed from the solid matter, and methanol (70ml) is added to the solid matter, which then is filtered, yellow solid matter (N,N'-Diphenyl-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine)(0.81g, 45%) is obtained.

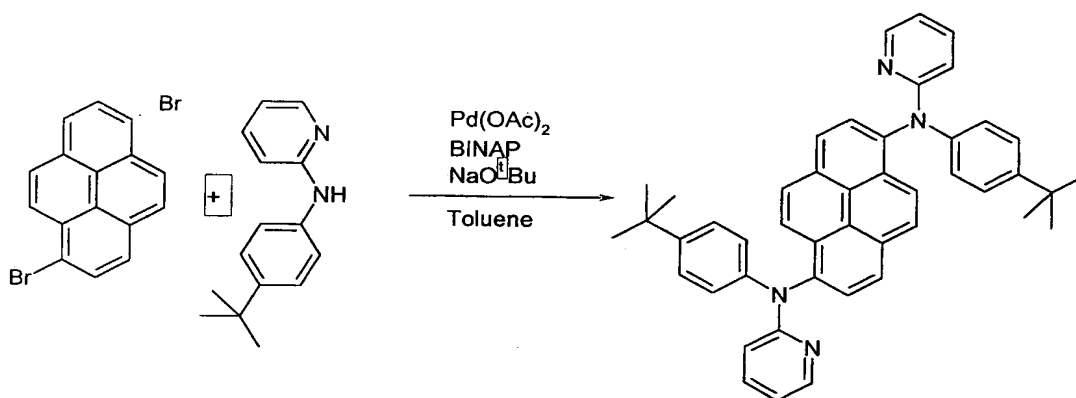
(7) Synthesis of (4-terr-Butyl-phenyl)-pyridin-2-yl-amine



(4-tert-Butyl-phenylamine) (1.2mL, 0.0076mol), (2-Bromo pyridine)(1mL, 0.01mol), BINAP (0.06g, 4%mol), Pd(OAc)<sub>2</sub>(0.02g, 3%mol) and NaO<sup>t</sup>Bu(1.5g, 0.016mol) are dissolved in toluene (50mL) in the 2-necks-r.b.f. so as to be refluxed for 24 hours. When the reaction is finished, the 2-necks-r.b.f. is cooled and toluene, that is,

reaction solvent is removed. Result material is extracted by using water and methylene chloride. methylene chloride is removed under decompression after water is removed by using  $\text{MgSO}_4$ . Silica gel short column is generated by methylene chloride, sediment is formed by using nucleic acid. When the sediment is filtered, white solid matter such as 4-tert-Butyl-phenyl)-pyridin-2-yl-amine (1.32g, 73%) is obtained.

(8) Synthesis of N,N'-Bis-(4-tert-butyl-phenyl)-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine

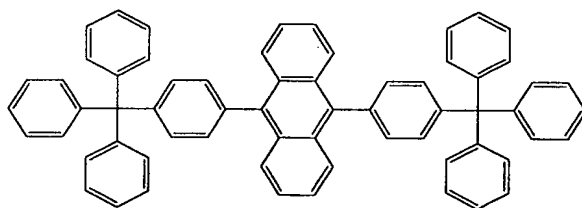


1,6-Dibromopyrene(1g, 0.0028mol), (4-tert-Butyl-phenyl)-pyridin-2-yl - amine(1.51g, 0.0067mol), BINAP(0.07g, 4%mol),  $\text{Pd}(\text{OAc})_2$ (0.02g, 3%mol) and  $\text{NaO}^t\text{Bu}$ (1.18g, 0.012mol) are dissolved in toluene (45mL) in the 2-necks-r.b.f. so as to be refluxed for 24 hours. When the reaction is finished, solid matter is generated. 50% of toluene is removed from the solid matter, which is then filtered after methanol (70mL) is added thereto. When the solvent is removed by silica gel short column by using methylene chloride, (N,N'-Bis-(4-tert-butyl-Phenyl)-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine)(0.99g, 60%) is obtained.

Hereinafter, a preferred embodiment of the organic electroluminescent device will be described according to the present invention.

## [Embodiment]

An indium tin oxide (ITO) glass is patterned so as to have a size of 3mm x 3mm. The patterned ITO glass is then cleaned. A substrate is loaded on a vacuum chamber of which basic pressure is set up as  $1 \times 10^{-6}$  torr, CuPC(200 Å), NPB(500 Å), a light-emitting layer (300 Å), Alq<sub>3</sub>(500 Å), LiF(5 Å), and Al(1,000 Å) are deposited on the ITO in order. In this case, material in a following drawing is employed as a first HOST of the emitting layer and a mixing ratio of the host and dopant is 1:0.01.



HOST-1

## [First embodiment]

When about 1mA of electric current is flown by using dopant having a chemical formula of S-26, brightness shows about 3.2cd/A, whereby CIE (Commision Internationale de L'Eclairage)  $x=0.146$ ,  $y=0.205$ .

## [Second embodiment]

When about 1mA of electric current is flown by using dopant having a chemical formula of S-28, brightness shows about 3.4cd/A, whereby CIE (Commision Internationale de L'Eclairage)  $x=0.15$ ,  $y=0.196$ .

## [Comparative embodiment]

ITO (Indium Tin Oxide) glass is patterned so as to have a size of 3mm x 3mm. The patterned ITO glass is then cleaned. A substrate is loaded on a vacuum chamber of which basic pressure is set up as  $1 \times 10^{-6}$  torr, and such an organic matters as

CuPC(200 Å), NPB(500 Å), emitting layer (300 Å), Alq<sub>3</sub>(200 Å), LiF(5 Å), and Al(1000 Å) are deposited on the ITO glass. When about 1mA of electric current is flown, brightness is about 1.8cd/A, whereby CIE (Commision Internationale de L'Eclairage) x=0.194, y=0.297.

#### **[EFFECT OF THE INVENTION]**

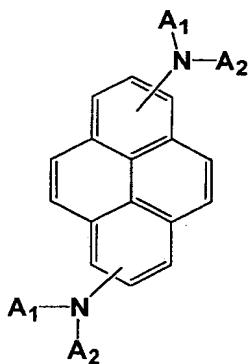
Accordingly, the present invention is a blue emitting material of an emitting layer and an organic electroluminescent device with blue color purity and a high luminescent efficiency is obtained by material with high color purity.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the spirit or scope of the inventions. Thus, it is intended that the present invention covers the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

**What is claimed is:**

1. An organic electroluminescent device in which an emitting layer is formed between an electron injected electrode (anode) and a hole injected electrode (cathode), the emitting layer comprising a blue emitting material realizing blue luminescence that is expressed by the following chemical formula 1:

[Chemical formula 1]



wherein, at least one of A<sub>1</sub> and A<sub>2</sub> is selected from a substituted or non-substituted aromatic group, a heterocyclic group, an aliphatic group and hydrogen.

2. The organic electroluminescent device of claim 1, wherein materials forming the emitting layer together with the material of the chemical formula 1 can be used solely or composed with more than one material, and a wt% of the material in the chemical formula 1 is 0.1 ~ 90wt% among a total weight of the emitting layer.

3. The organic electroluminescent device of claim 2, wherein the material to be composed to the material in the chemical formula 1, for being used as a luminescent layer, is selected from a substituted or non-substituted fused aromatic group.

4. The organic electroluminescent device of claim 3, wherein the substituted or non-substituted fused aromatic group is selected from a group consisting of naphthalene, anthracene, phenanthrene, pyrene, perylene, quinoline and acridone.

5. The organic electroluminescent device of claim 3, wherein the substituted fused aromatic group is selected from a group consisting of aryl, arylallyl, allyl, alkyl, alkoxy, aryloxy and arylamino.

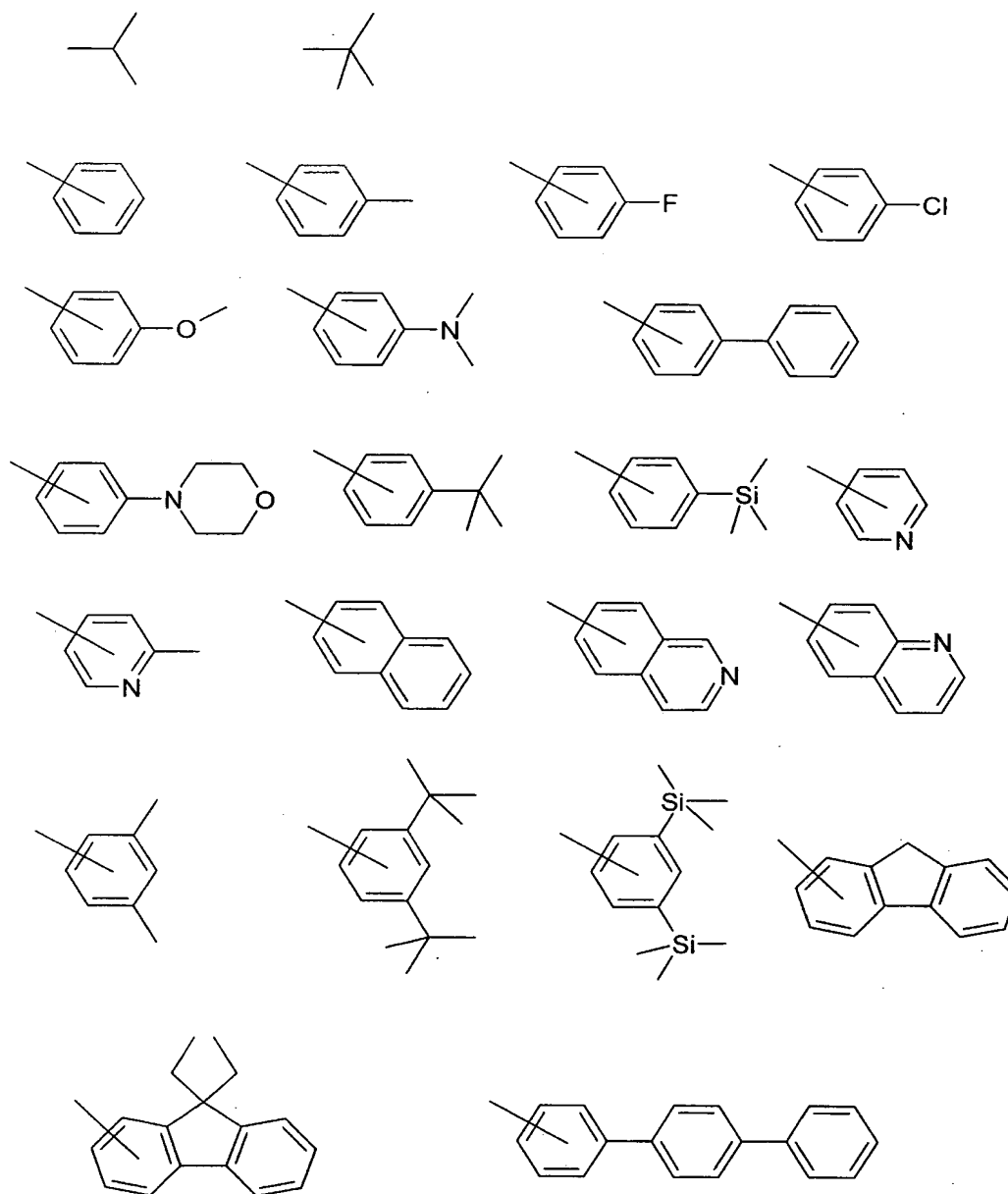
6. The organic electroluminescent device of claim 1, wherein at least one of an A1 and A2 is selected from phenyl, biphenyl, pyridyl, naphthyl, quinolyl, isoquinolyl, fluorenyl, terphenyl, methyl, ethyl, propyl and isopropyl.

7. The organic electroluminescent device of claim 1, wherein a substituent of each substituted A1 and A2 is selected from the substituted group consisting of aryl, aryloxy, alkoxy, alkyl, alkylamino, hydroxyl, amino, halogen, carbonyl, amide, alkylsilyl, arylsilyl and carboxylic, respectively.

8. The organic electroluminescent device of claim 1, wherein a substituent of each substituted A1 and A2 is selected from a group consisting of phenyl, phenoxy, tolyoxy, vinyl, aldehyde, methyl, ethyl, propyl, isopropyl, t-butyl, cyclohexyl, diphenylamino, methoxy, ethoxy, propoxy, butoxy, dimethylamino, trimethylsilyl, triphenylsilyl, fluorine and chlorine.

9. The organic electroluminescent device of claim 1, wherein at least one of the A1 and A2 in one of following chemical formula 4.

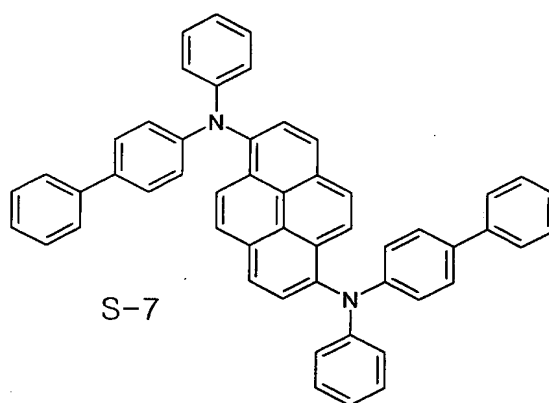
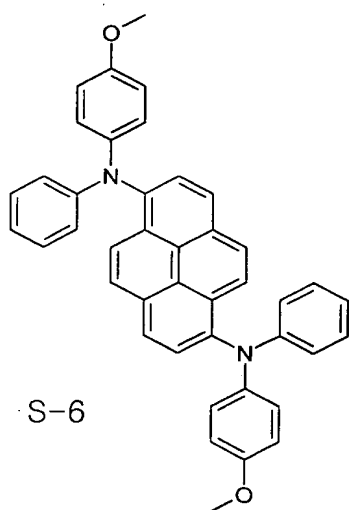
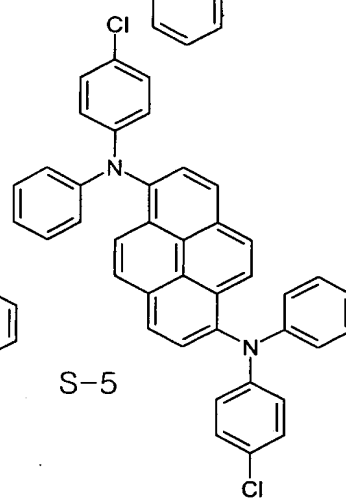
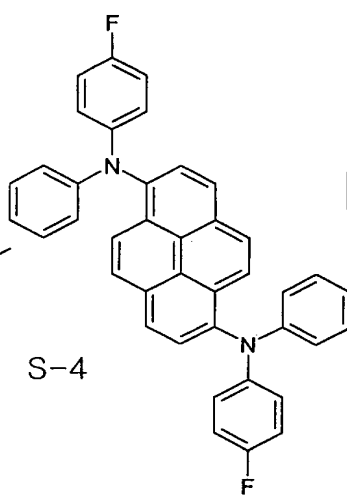
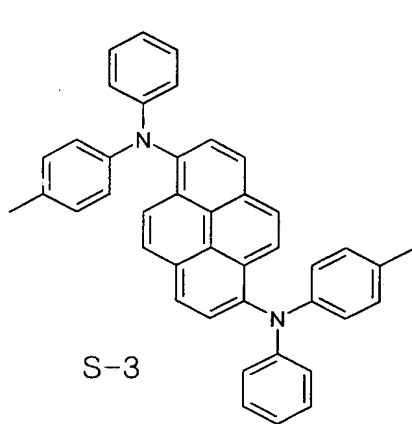
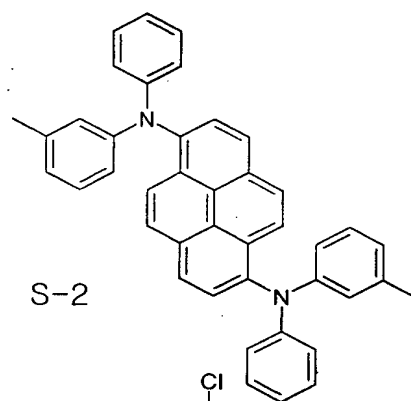
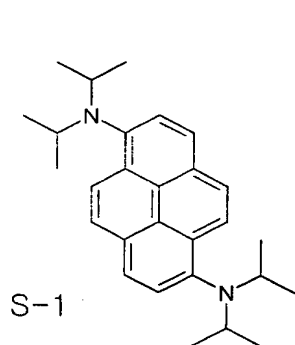
[Chemical formula 4]

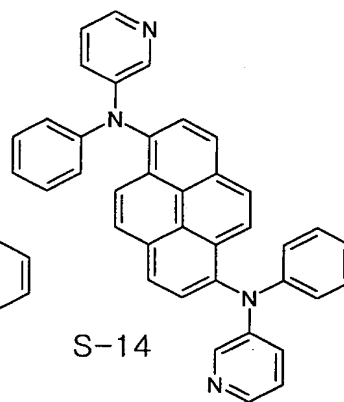
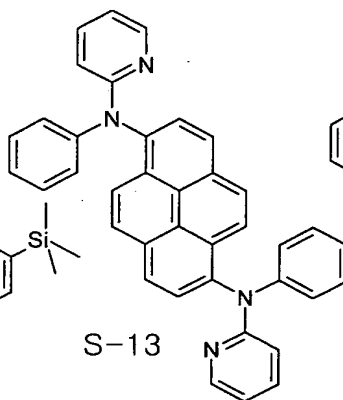
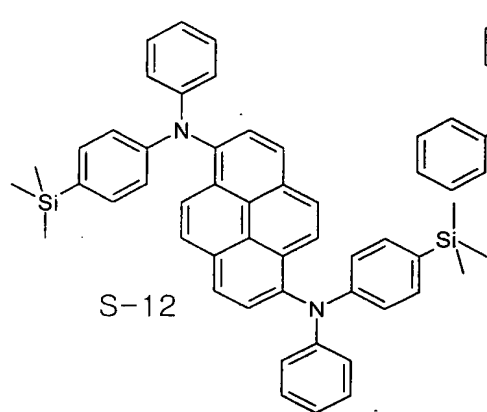
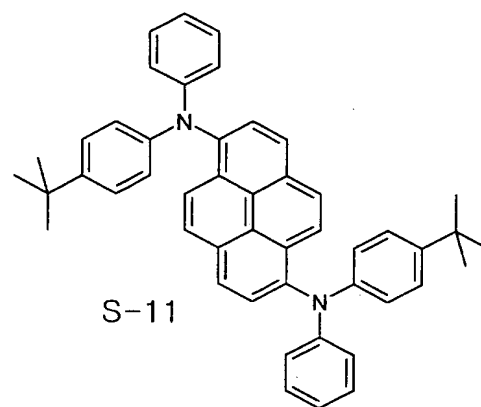
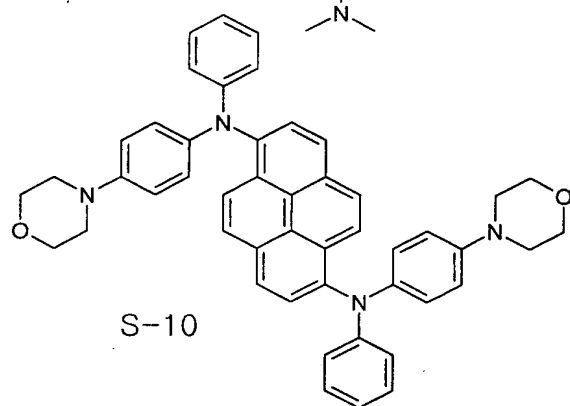
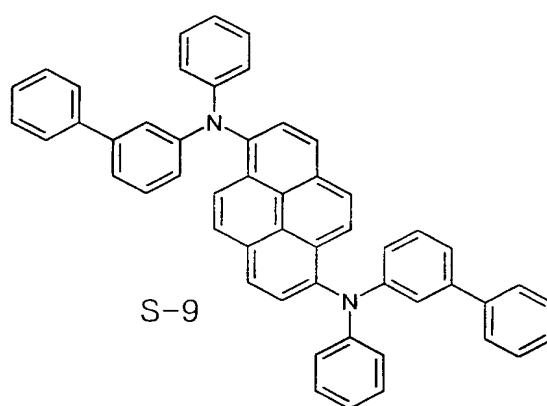
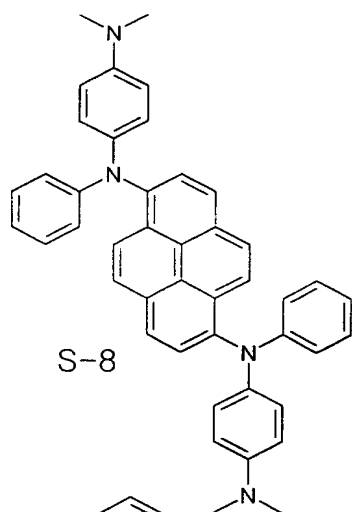


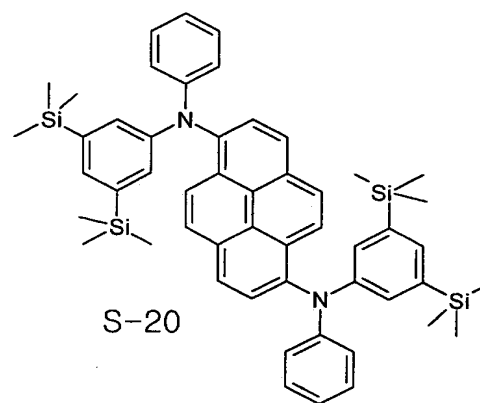
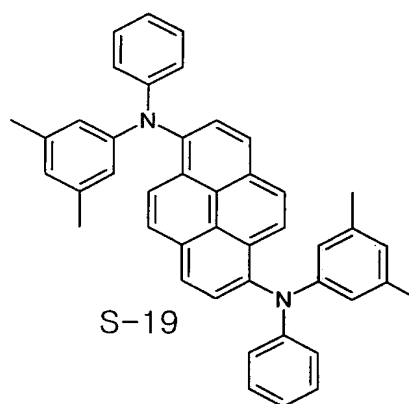
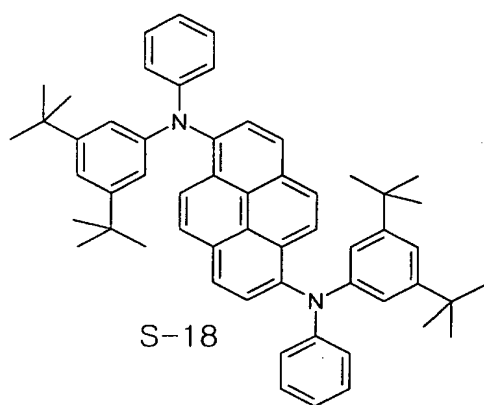
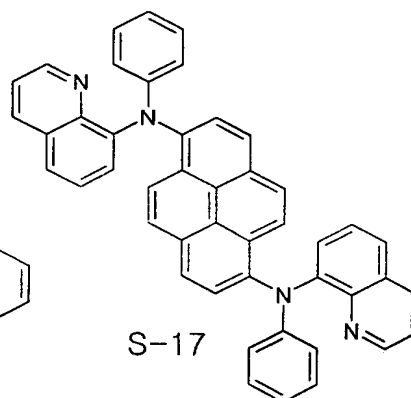
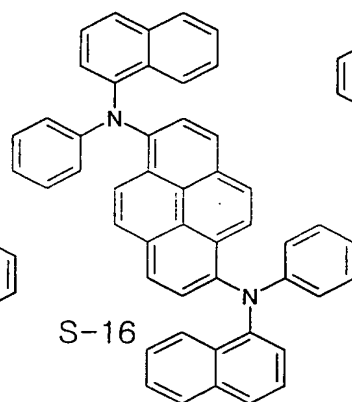
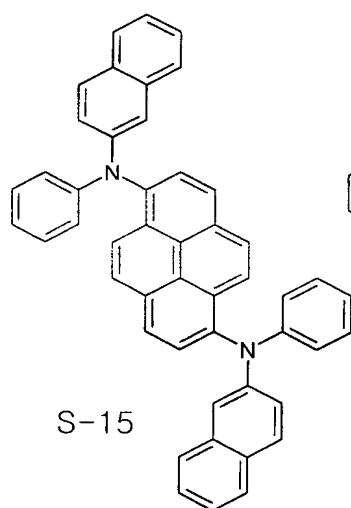
10. The organic electroluminescent device of claim 1, wherein the blue emitting material is at least one of following chemical formula 5.

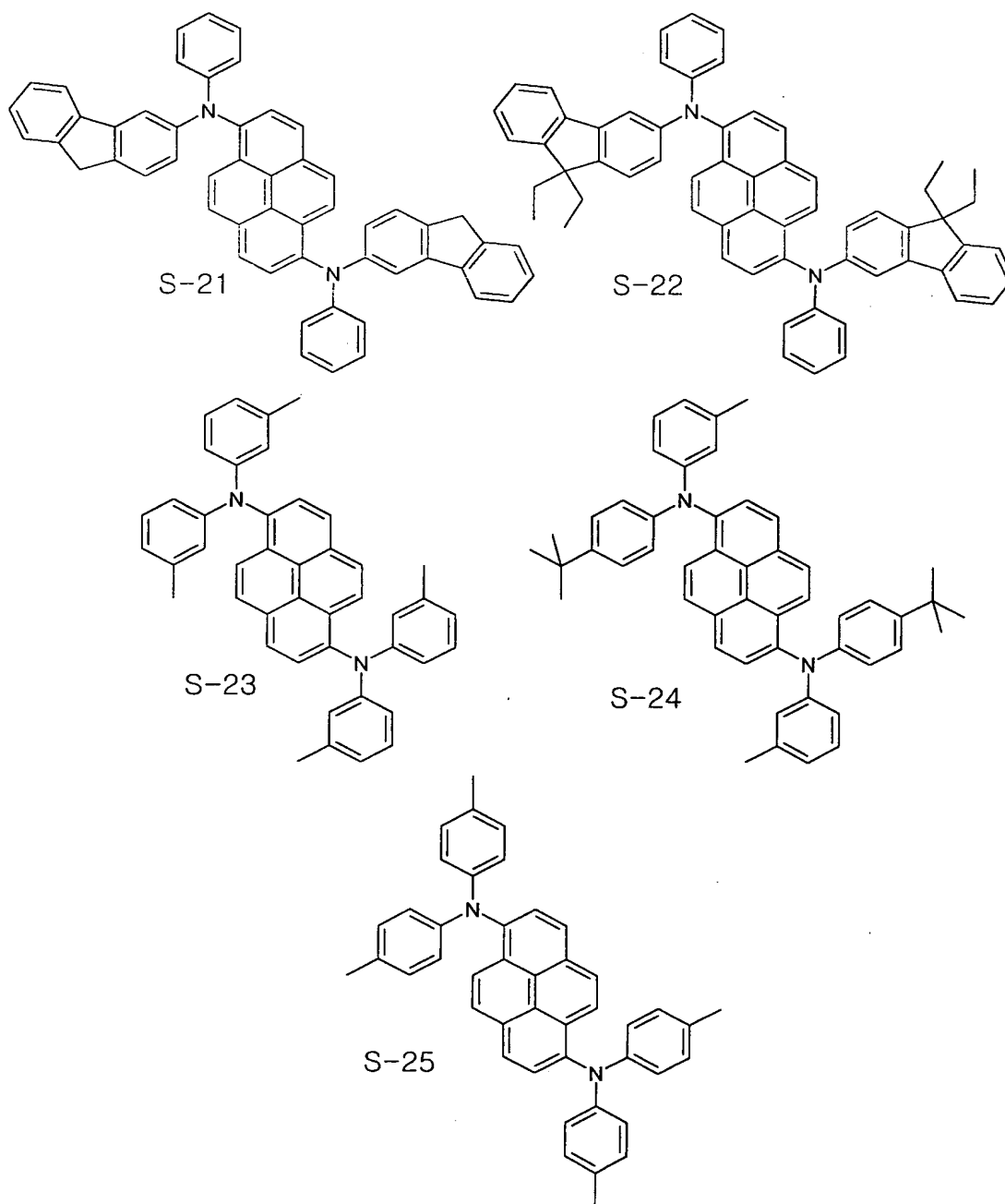
[Chemical formula 5]

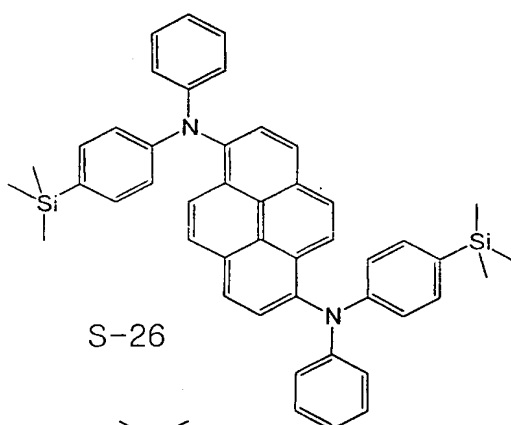




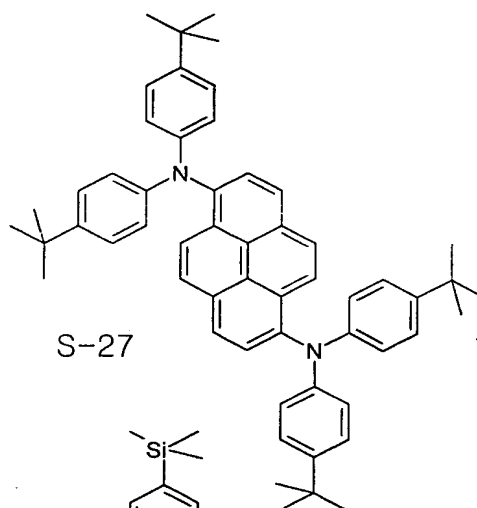




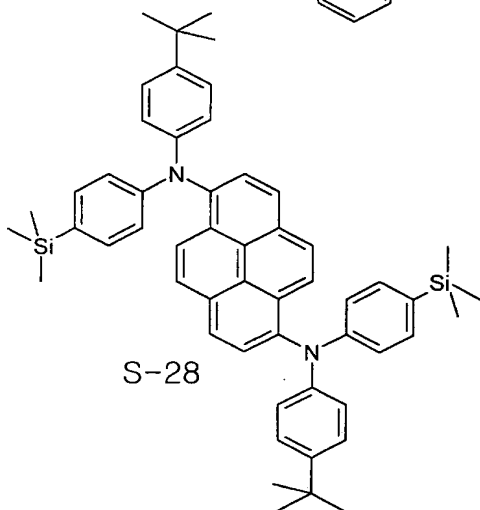




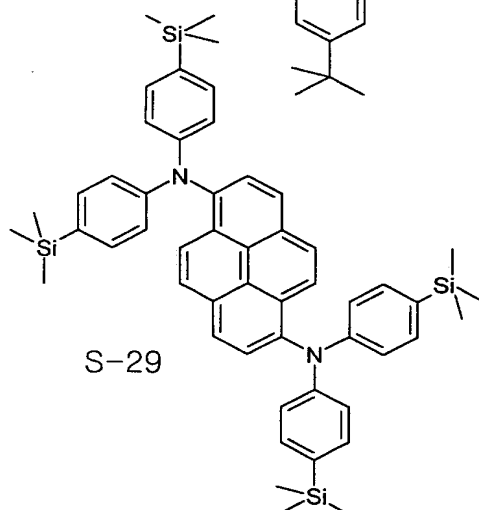
S-26



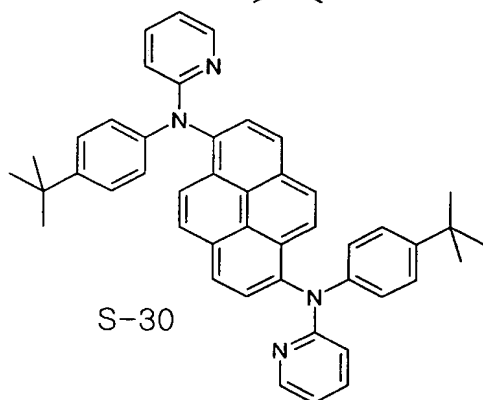
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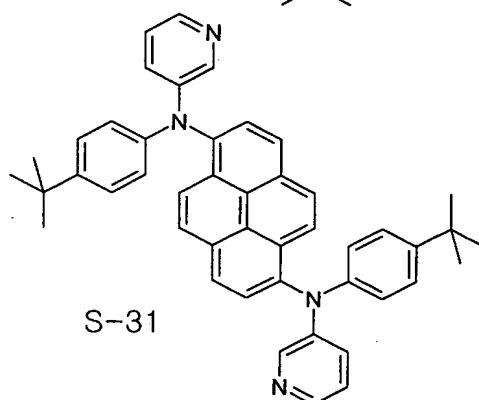
S-28



S-29



S-30



S-31

